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13. ABSTRACT *(Maximum 200 words)*

The work performed in FY90 consisted of 5 separate projects: 1) laser ignition of H_2/O_2 and D_2/O_2 premixed gases through resonant multiphoton excitation of H and D atoms, 2) spectral characterization of laser-generated microplasma emission from fuel molecules, 3) modeling of the laser ignition phenomenon, 4) development of a new flame thermometer based on multiphoton excitation of NO, and 5) investigation of CO photolysis at 193 nm.

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FINAL REPORT FOR AIR FORCE OFFICE OF SCIENTIFIC RESEARCH
CONTRACT No. 90-0025

Contract Title: Fundamental Studies of Laser Ignition and Kinetics in Reactive Gases

Contract Period: 1 October 1989 to 30 September 1990

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SUMMARY

The work performed in FY90 consisted of 5 separate projects: 1) laser ignition of H_2/O_2 and D_2/O_2 premixed gases through resonant multiphoton excitation of H and D atoms, 2) spectral characterization of laser-generated microplasma emission from fuel molecules, 3) modeling of the laser ignition phenomenon, 4) development of a new flame thermometer based on multiphoton excitation of NO, and 5) investigation of CO photolysis at 193 nm.

I. Laser Ignition of H_2/O_2 and D_2/O_2 Premixed Flows

Laser ignition experiments involving the hydrogen atom 2-photon resonance at 243 nm have been conducted and show an interesting isotope wavelength dependence.[1,2] Figure 1 shows the ILE dependence for the ignition of H_2/O_2 (curve a) and D_2/O_2 (curve b) using a tunable laser near 243 nm. The plots clearly show a wavelength shift which corresponds to 22 cm^{-1} at the two-photon level. This is exactly the energy difference in the n=2 excited state for the two different isotopes. Previously, we observed a similar wavelength dependence for the formation of microplasmas in flows of pure H_2 and D_2 gases. Figure 2 shows the ignition ILE dependence on equivalence ratio for H_2/O_2 (Figure 2a) and D_2/O_2 (Figure 2b) with the laser set at the corresponding minimum wavelength points (Figure 1) which are the wavelengths for maximum two-photon excitation. As can be seen, the two curves are basically alike as would be expected for these two fuel gases whose flame chemistry is quite similar.

Publications:

1. B.E. Forch and A.W. Miziolek, **Proceedings of the 27th JANNAF Combustion Meeting**, Nov. 90 (in press).
2. B.E. Forch and A.W. Miziolek, **Comb. and Flame**, 1991 (in press).

II. Laser-Produced Microplasma Emission From Fuel Molecules

An important question which thus far has remained unanswered pertains to the degree to which the species-specific microplasma chemistry influences the growth and behavior of the ignition kernel. We are attempting to address this question by studying the microplasmas in more detail, i.e. specifically by trying to determine their chemical composition. Figure 3 shows the microplasma emission spectra from two different fuel target molecules, i.e. propane (Figure 3a) and benzene (Figure 3b), using the ArF excimer laser.[3] Clearly,

there are major differences in the formation of excited fragments in the microplasmas for these two molecules and, therefore, we expect that the subsequent ignition chemistry should be different as well. A particularly important, but difficult, goal to reach would be to fully characterize the laser-produced microplasmas with respect to the size, temperature, as well as major and minor reactive species which constitute a viable ignition kernel. Figure 4 shows preliminary results taken from a recently acquired streak camera (Hamamatsu Model C1587) of a laser-produced microplasma in a H_2/O_2 flow. This apparatus will be particularly useful for time-resolved spatial and spectroscopic studies of microplasma production and evolution.

Publications:

3. R.J. Locke, J.B. Morris, B.E. Forch, and A.W. Miziolek, **Appl. Opt.**, 29, 4987, 1990.

III. Modeling of Laser Ignition of Reactive Gases

Previous modeling efforts of laser ignition have involved a fluid dynamic description of blast wave evolution and heating, as well as a more complete model which includes some level of detailed chemistry. However, to the best of our knowledge, a robust and well-tested model of laser ignition that can be used as a predictive tool currently does not exist. Our approach is to write a one-dimensional time-dependent code which describes the creation of the laser-induced kernel, as well as the time and spatial development of the system from laser-irradiation, to ignition, and finally to extinction.

Specifically, the new code that is being written includes the basic equations, those of continuity, continuity of the individual species, diffusion, motion, and energy balance, in one spatial dimension and time.[4] The code utilizes the Chemkin II package, i.e. the thermodata and transport data sets (with our additions and alterations) and several of the thermodynamic and math algorithms. The set of time-dependent partial differential equations is solved using IMSL's DMOLCH, a finite element code which uses the method of lines with cubic Hermite polynomials. Physically, we assume the laser heats a spherical (cylindrical) kernel. The laser-induced heating is modeled by including a time and spatial dependent source term in the energy equation. The form of this term is chosen to fit the time-dependent luminescent data obtained from the streak camera (as in Figure 4). From this input the code will model the time and radial dependencies of the temperature, density, pressure and species concentrations in the system. The results, when finally available, will be compared with temperature and species data obtained from time-resolved pump-probe experiments.

Publications:

4. N.M. Witriol, B.E. Forch, and A.W. Miziolek, **Proceedings of the 27th JANNAF Combustion Meeting**, Nov. 90 (in press).

IV. Multiphoton Excitation Studies of NO for Flame Thermometry

During the process of determining the primary photoproducts in the above study, we realized the importance of developing diagnostics for species, such as NO, whose single-photon excitation falls far in the ultraviolet region (220 nm) and thus may suffer from the coincident perturbation (photolysis) of other species such as NO_2. This perturbation, of course, leads to artificially high levels of NO. Our approach of two-photon excitation of the NO (A) state at 452

nm was inspired by Professor T.A. Cool of Cornell University, who pioneered this method for flame NO detection. Figure 5 shows a Resonance Enhanced Multiphoton Ionization (REMPI) spectrum of the $O_{22} + P_{12}$ branch taken in a $C_2H_4/O_2/Ar$ flame containing 1% NO.[5] A spectral simulation yields a temperature of 1169+/-50 K, which is in fair agreement with the temperature (1000 K) measured with a coated thermocouple. Figure 6 shows a two-photon LIF spectrum of NO taken at room temperature. As one can see, the spectral best-fit simulation yields a temperature of 326 K. Both the high temperature and room temperature results are encouraging, but indicate that significant improvements are still needed before this approach can be utilized as an alternate/additional flame thermometer. In particular, improvements are needed in spectroscopic constants and in transition probabilities.

Publications:

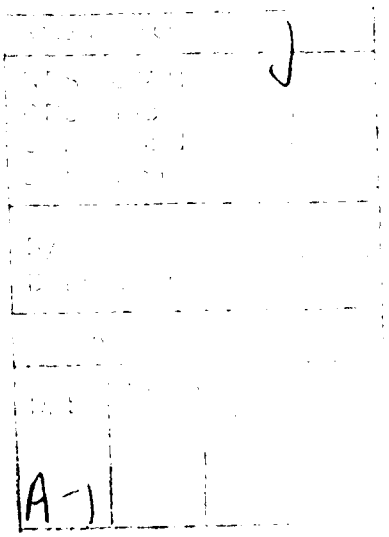
5. R.C. Sausa, S.L. Howard, R.J. Locke, A.J. Kotlar, and A.W. Miziolek, Fall Meeting of the Eastern Section: The Combustion Institute, 1990.

V. Photodissociation Studies of CO at 193 nm

The ArF excimer laser (193 nm) was used to photolyse the CO molecule and ground-state oxygen atoms were detected with a probe laser by two-photon laser induced fluorescence.[6] The slope of a ln-ln plot of the fluorescence signal intensity vs laser photolysis energy yields n=1.90+/-0.09, which indicates a quadratic dependence on the 193 nm photolysis of CO. A mechanism has been proposed where the initial absorption of one ArF photon produces CO in the excited (a) state, which subsequently absorbs one additional ArF photon into a dissociative state with suspected triplet character. A similar study in which the oxygen and carbon photoproducts have been detected using resonance multiphoton ionization (REMPI) has also yielded a quadratic photolysis dependence as well as the nascent spin-orbit states of the oxygen photofragment.[7]

Publications:

6. C.N. Merrow and B.E. Forch, J. Chem. Phys., 93, 4791, 1990.
7. B.E. Forch and C.N. Merrow, J. Chem. Phys., (submitted).



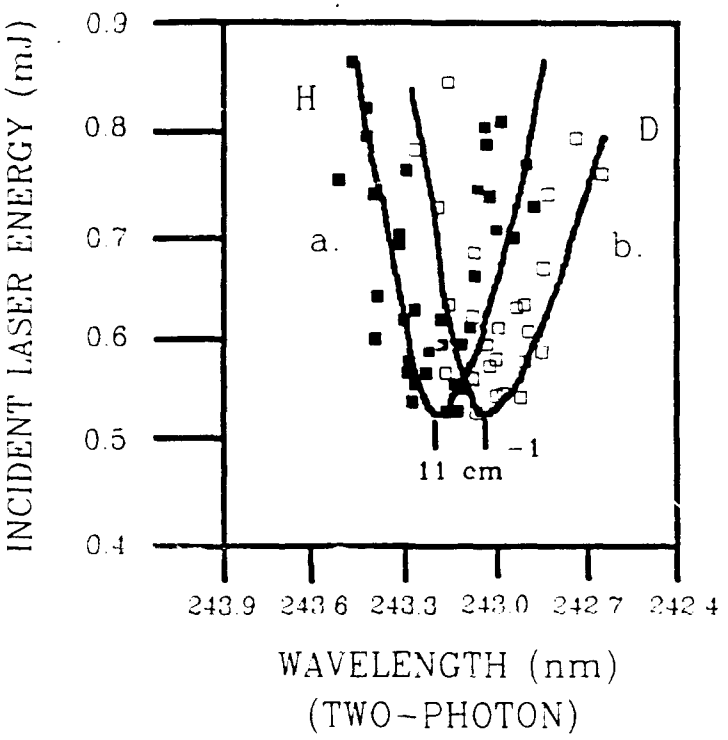


FIGURE 1. ILE NECESSARY TO IGNITE PREMIXED FLOWS OF: a. H_2/O_2 AND b. D_2/O_2, AS A FUNCTION OF EXCITATION WAVELENGTH NEAR 243 nm. A SHIFT OF +11 cm^{-1} OF IGNITION CURVE b. RELATIVE TO IGNITION CURVE a. IS EVIDENT.

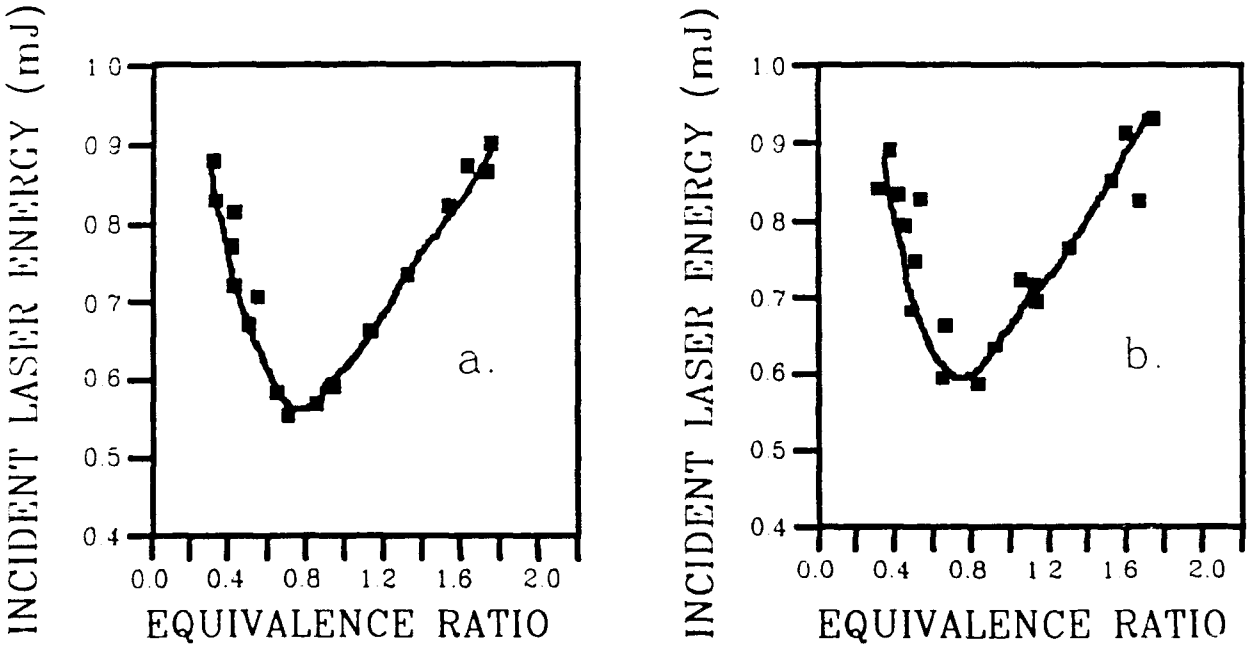


FIGURE 2. DEPENDENCE OF THE ILE REQUIRED TO IGNITE PREMIXED FLOWS OF: a. H_2/O_2 AND b. D_2/O_2, AS A FUNCTION OF EQUIVALENCE RATIO. THE LASER WAS SET AT THE PEAK OF THE TWO-PHOTON EXCITATION WAVELENGTH OF: a. H-ATOMS AT 243.07 AND b. D-ATOMS AT 243.00 nm.

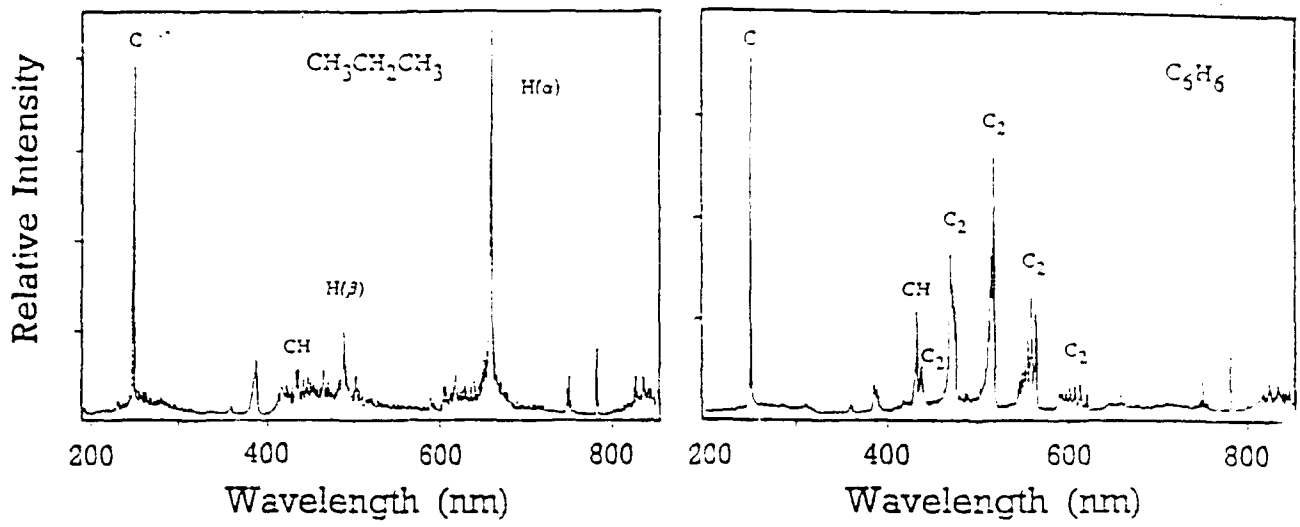


FIGURE 3. ArF LASER PRODUCED MICROPLASMA EMISSION SPECTRA FOR PROPANE (LEFT) AND BENZENE (RIGHT).

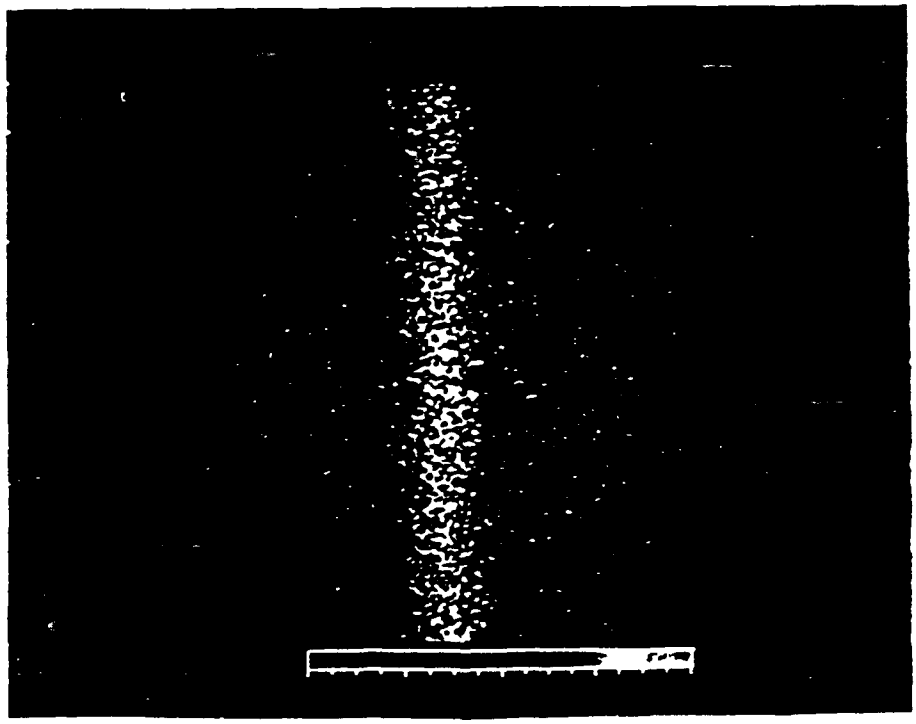


FIGURE 4. STREAK CAMERA TRACE FROM AN ArF LASER PRODUCED MICROPLASMA FORMED IN A PREMIXED H_2/O_2 FLOW: FULL SWEEP EQUALS 3 ns.

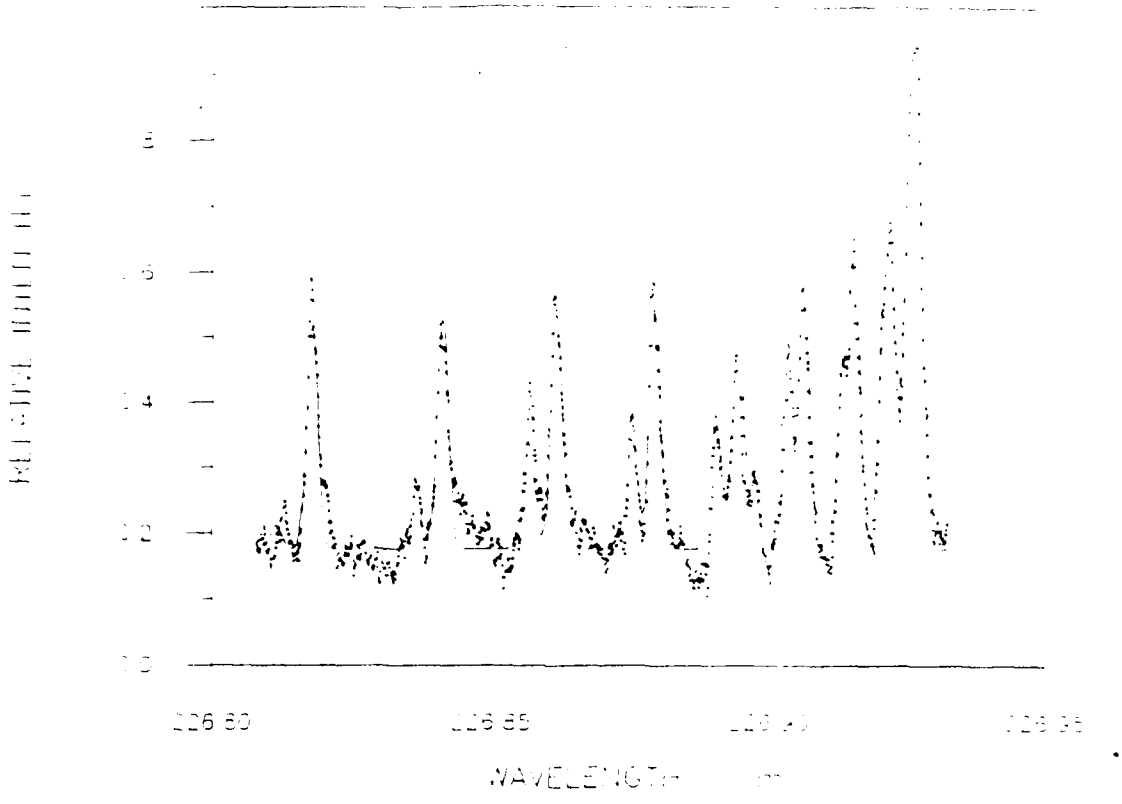


Figure 5. REMPI (2+2) spectrum of the NO $O_{22}+P_{12}$ branch (T=1169+/-50K)

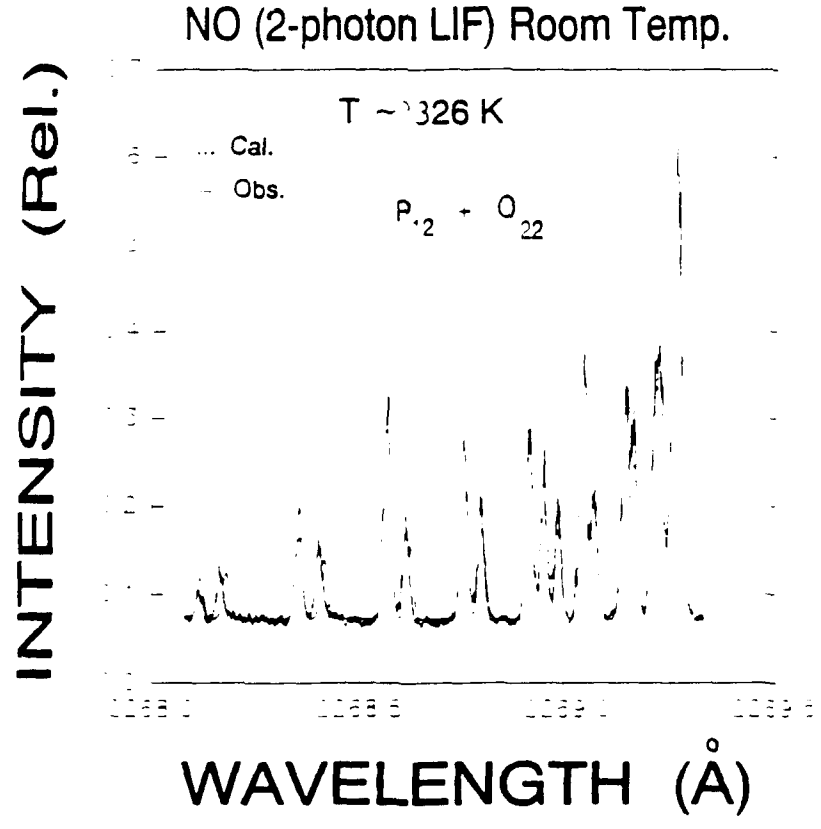


Figure 6. Two-photon LIF of NO at room temperature